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Supplementary Information

Three-dimensional covalent organic framework membrane for efficient proton conduction

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Experimental

Materials

Tetrakis(4-aminophenyl) methane was purchased from Energy Chemical. P-phthalaldehyde and 36% acetic acid were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Etidronic acid was purchased from Bide Pharmatech Ltd. All regents and solvents were used as received.

Preparation of three-dimensional (3D) COF membranes

3D COF (COF-300) membranes were prepared by interfacial polymerization method. Typically, 80 mg Tetrakis(4-aminophenyl) methane was added into 20 ml acetic acid aqueous solution (6.4 ml 36% acetic acid and 13.6 ml deionized water); 48 mg P-phthalaldehyde was added into 8 ml mesitylene and sonicated until complete dissolution. Afterwards, amine monomer solution was poured into the bottom of 100 ml glass beaker and then aldehyde monomer solution was dropped carefully on the top of amine monomer solution. Then the glass beaker was sealed and put into a 65 °C oven for 24 h without any disturbance. The membrane formed at the interface was taken out carefully and washed with N, N-Dimethylformamide, 1,4-dioxane to remove any unreacted monomers. Finally, the obtained membrane was soaked into ethanol for the next treatment and characterization.

Preparation of 3D COF membranes loaded with etidronic acid

Typically, the obtained COF-300 membrane was immersed into 20 ml etidronic acid ethanol solution (1 g/20 mL) for 48 h and then washed with copious amounts of water to obtain the etidronic acid@COF-300 membrane.

Characterizations and measurements

Characterizations

Powder X-ray diffraction (PXRD) was performed on a Rigaku D/max 2500v/pc diffractometer. Prior to PXRD analysis, membrane samples soaked into ethanol or water were prepared to study the structural difference. Fourier transform infrared (FT-IR) spectra (400 to 4000 cm^{-1}) were acquired using a BRUKER Vertex 70 spectrometer equipped with ATR Diamond. The solid-state ^{13}C nuclear magnetic resonance (NMR) spectrum was acquired on a Bruker 600 MHz NMR spectrometer (JEOL JNM ECZ600R). Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) images were observed from field emission scanning electron microscope (Nanosem 430) and HRTEM (Tecnai G2 F20), respectively. Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere using

Netzsch TG 209 F3 and the heating rate was 10 °C/min (40 to 800 °C). The Young's modulus experiments were performed on a BRUKER Dimension Icon atomic force microscopy.

Measurements

The swelling ratio was calculated from the difference in membrane surface area between dried and fully hydrated state as follows:

$$\text{Swelling ratio}\ (\%) = \frac{A_{wet,\,w} - A_{dry}}{A_{dry}} \times 100\% \quad (2)$$

where $A_{wet,\,w}$ and A_{dry} are the membrane area (cm^2) of fully hydrated and dried state, respectively.

The proton conductivity of membrane samples was tested using a two-point-probe method, performing on an electrochemical workstation (FRA, IVIUM Tech). The membrane samples were put inside a thermos-hygrostat where the temperature and relative humidity (RH) could be changed. The proton conductivity (σ, S cm^{-1}) was calculated as follows:

$$\sigma = \frac{l}{AR} \quad (3)$$

where l (cm) represented the distance between the electrodes, A(cm^2) was referred to the cross-section area and R(Ω) was the Ohmic resistance of the membranes.

The activation energy (E_a, kJ mol^{-1}) was calculated as follows:

$$\ln \sigma = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln \sigma_0 \quad (4)$$

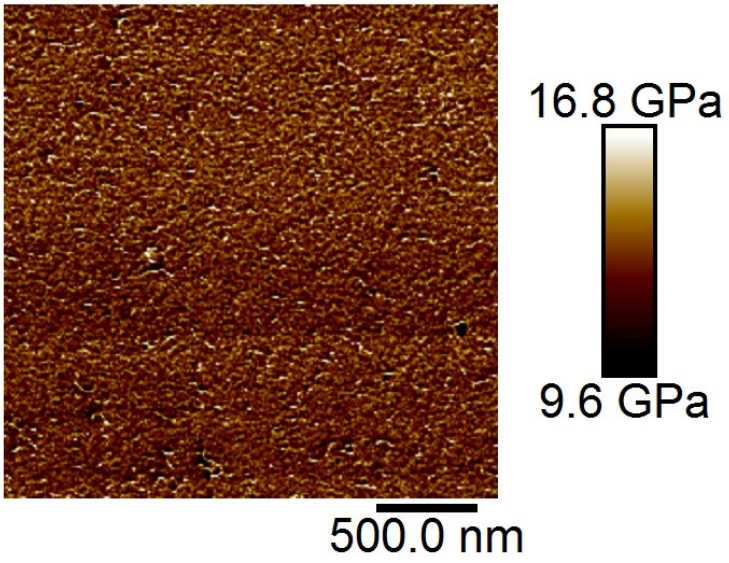

Fig. S1 Measurement of mechanical property of the COF-300 membrane from AFM.

Table S1 Comparison of proton conductivity between previously reported COF materials and this work

Sr. No	System	Proton conductivities (S cm^{-1})	Measurement conditions	Ref.
1	etidronic acid@COF-300	6.50×10^{-1}	90 °C, 100% RH	This work
2	Im@Py-TT-COF-50	3.08×10^{-3}	130 °C, anhydrous	1
3	PTSA@TpAzo	7.8×10^{-2}	80 °C, 95% RH	2
4	H3PO4@NKCOF-1	1.13×10^{-1}	80 °C, 98% RH	3
5	H3PO4@TPB-DABI-COF	1.52×10^{-1}	160 °C, anhydrous	4
6	tra@EB-COF	3.25×10^{-3}	160 °C, anhydrous	5
7	PA@Tp-Azo	9.9×10^{-4}	59 °C, 98% RH	6
8	COF-F6-H	4.2×10^{-2}	140 °C, anhydrous	7
9	im@TPB-DMTP-COF	4.37×10^{-3}	120 °C, anhydrous	8
10	H_3PO_4@TPB-DMeTP-COF	1.91×10^{-1}	160 °C, anhydrous	9
11	H3PO4@NKCOF-10	6.97×10^{-2}	25 °C, 90% RH	10
2	Phytic@TpPa-(SO_3H-Py)	5×10^{-4}	120 °C, anhydrous	11
3	PA@TpBpy-MC	2.5×10^{-3}	120 °C, anhydrous	12
4	RT-COF-1AcB	5.25×10^{-4}	40 °C, 100% RH	13
5	EBCOF: PW_{12}	3.32×10^{-3}	25 °C, 97% RH	14
9	NUS-10(R)	3.96×10^{-2}	25 °C, 97% RH	15
13	BIP	3.2×10^{-2}	95 °C, 95% RH	16
14	aza-COF-2_H	4.80×10^{-3}	50 °C, 97% RH	17
17	IPC-COF	3.8×10^{-1}	80 °C, 100% RH	18
19	SCOF	5.4×10^{-1}	80 °C, water	19

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